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BINDER MODEL SYSTEM TO BE USED FOR DETERMINATION OF PREPOLYMER FUNCTIONALITY

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ABSTRACT

The recording viscometer method, developed previously, has been further improved and modified. The method has been applied to the reactions of model compounds, and the results obtained correspond closely with the expected values.

Preliminary tests have also been carried out on a number of carboxy- and hydroxy-terminated prepolymers. The results indicate that the recording viscometer technique can be used to determine the functionality of most prepolymers, including unsaturated ones.

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I OBJECTIVES

The objective of this work is to develop a method for determining functionality in prepolymers used for rocket binders. Earlier work had shown that for carboxy- and hydroxy-terminated prepolymers the esterification reaction is the most satisfactory for our studies. Thus the present report period was concerned with developing methods for studying this reaction in both model compounds and prepolymers.

II INTRODUCTION

Work at the Jet Propulsion Laboratories by H. E. Marsh and J. J. Hutchison* has shown that a method for determining the functionality distribution of prepolymers can be derived by extending Flory's network theory.[1] Since this requires a reaction that goes to completion with no significant side reactions, these workers selected esterification as the best means of crosslinking hydroxy- and carboxy-terminated prepolymers. However, the results obtained were not always consistent with theory. The main difficulty was that the polymerization conditions selected required long reaction times, even at high temperatures, to reach the degree of completion necessary for functionality determination. At these temperatures even the saturated prepolymers darkened considerably and unsaturated prepolymers were extensively decomposed. Other problems were that prepolymer and curing agents did not mix properly, and some of the more volatile components appeared to be lost during the reaction. Also, the incipient gel point was arbitrarily chosen as the point at which no noticeable flow occurred at 170°C.

Work done during the previous report period indicated that the use of model reactions other than esterification was not very promising.

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*For an abstract of the mathematics involved, see Appendix I.

However, the speed of the esterification reaction has been greatly improved by use of vigorous stirring and a strong nitrogen flow, so the problems associated with the previous work have been overcome. Furthermore, development of the stirred reactor technique made possible a continuous study of the changes in viscosity of the reaction mixture and provided the vigorous stirring necessary to complete the reaction. Preliminary results obtained with this system have shown that there is a very great increase in the viscosity of the prepolymer mix at the point where theory indicates that the mixture should start to gel; the system thus provides a means of determining the point of incipient gelation.

III DISCUSSION

A. Apparatus

It can be shown[2] that a large viscosity change must occur at the incipient gel point of a molten polyester gel system, since at this point infinite chains are possible.[1,3] Thus, an instrument was designed and built which would continuously record the viscosity of a reacting gel mixture. It was based on the principle of the Brookfield viscometer wherein one concentric cylinder is rotated within another and the force required to drive the inner cylinder is continuously monitored.

From the definition of viscosity, it can be shown[4] that, for two concentric cylinders,

$$\eta = \frac{F \cdot \Delta R}{4\pi^2 R^2 H V} \tag{1}$$

where η is the viscosity in poises, R is the radius of the moving cylinder in centimeters, H is its height, V is its speed in revolutions per second, F is the force needed to drive it in dynes, and ΔR is the difference in radii of the two cylinders. For our work, a dc motor was used to drive a small Teflon cylinder within a glass cylinder; various sizes for both the Teflon and glass cylinders could be chosen for different viscosity ranges. The field and armature of the motor were held at constant voltage by two regulated power supplies. Under these conditions, the torque delivered by the motor is

$$G = ki \tag{2}$$

where G is the torque in dyne-centimeters, k is a constant of the motor, and i is the current drawn. Since

$$G = FR, \tag{3}$$

equation (1) becomes

$$\eta = \frac{G \cdot \Delta R}{4\pi^2 R^3 H V} \qquad (4)$$

and from (2) we find

$$\eta = \frac{k}{4\pi^2} \left(\frac{\Delta R}{R^3 H}\right) \frac{i}{V} \qquad (5)$$

or more simply

$$\eta = k'k'' \left(\frac{i}{V}\right) \qquad (6)$$

where k'' is determined by the geometry of the system.

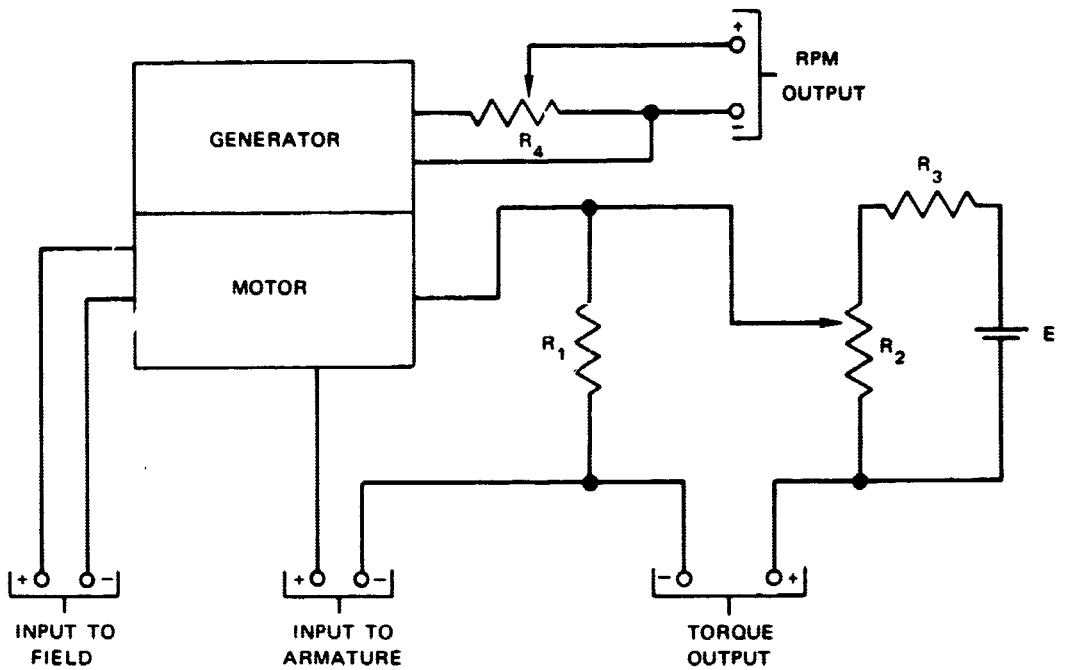
Because of the last term in equation (6), it was necessary to monitor both the speed and the current drawn by the motor. A small gear-driven generator whose output is directly proportional to the motor RPM was employed, and the current was determined by measuring the potential across a resistor in series with the armature (see Fig. 1). Both the speed and current were recorded on an X_1-X_2 millivolt recorder.

B. Determination of Gel Point

Work with the stirred reactor apparatus (Figs. 1 and 2) has shown that in order to obtain useful results a number of factors have to be balanced. Some of these factors and their influence are shown in Table I. At the present time a compromise procedure and apparatus have been decided upon, but they are by no means the ideal ones for all samples.

The procedure consists of preparing a prepolymer mix having known ρ (ratio of trifunctional carboxyl to total carboxyl) and known r (ratio of alcohol to acid) and determining the final viscosity of this solution. This procedure is repeated for a series of r values at constant ρ, and the r value at which gelation first takes place is noted. The functionality can then be calculated from this ρ and r.

We have recently introduced a change which has considerably shortened the time required for this series of experiments. Instead of preparing



R_1: 1 Ω 10W

R_2: 10k Ω 2W

R_3: 3.5k Ω 1/8 W

R_4: 10k Ω 2W

E: 1.35V MERCURY CELL

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Figure 1 SCHEMATIC OF THE RECORDING VISCOMETER

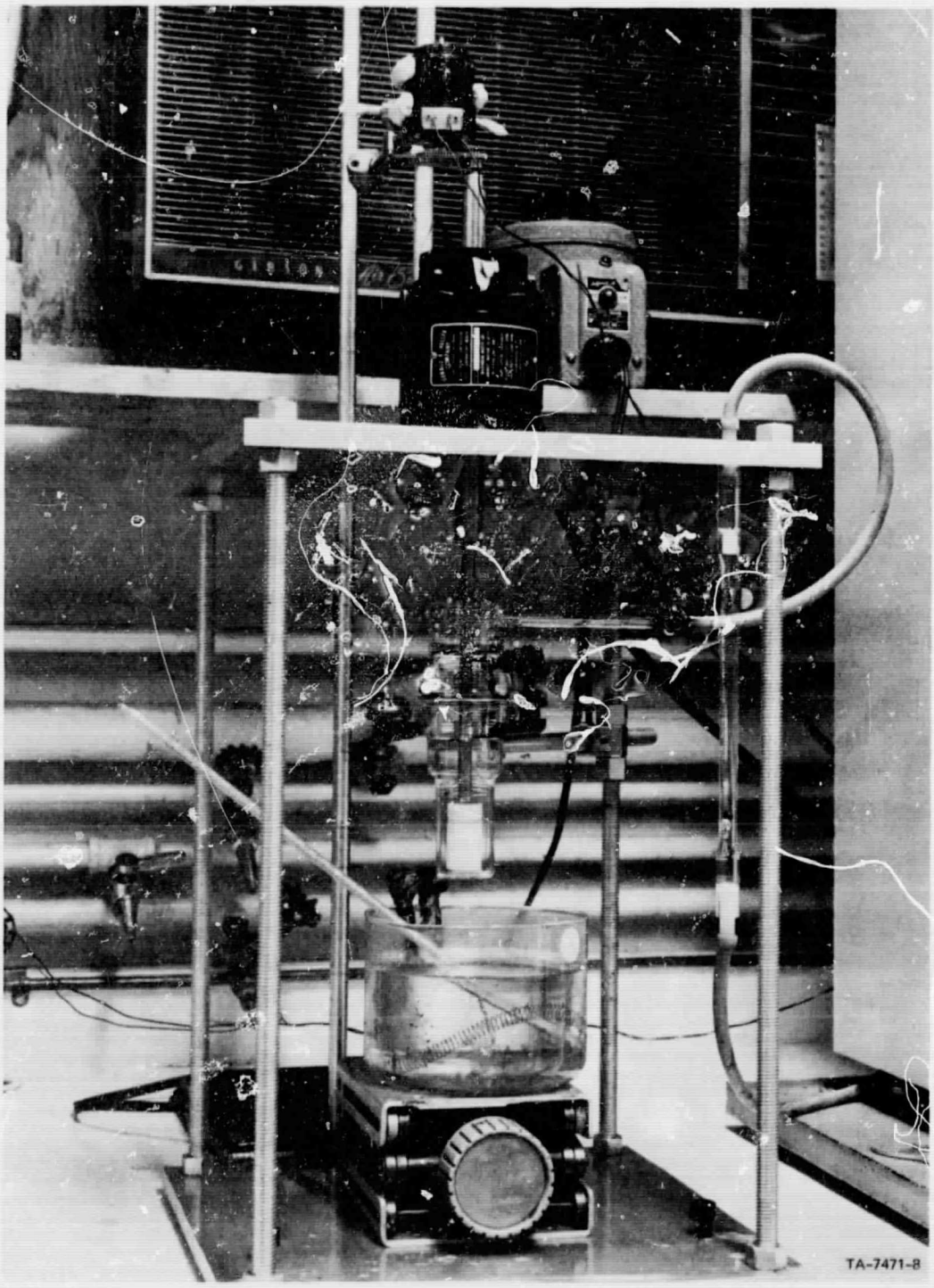

Figure 2 RECORDING VISCOMETER

Table I

Experimental Parameters Investigated	Advantages	Limiting Factors
Changes in rate of stirring or use of high speed synchronous motor	Increase speeds up reaction rate	High speed motors have too low response to increased torque
Temperature	Increase speeds up reaction and aids in the elimination of water	Decomposition of reagents, especially unsaturated compounds
Changes in quantity of material used, determined by changes in the size of the vessel	Smaller amounts gave faster reaction rate; less waste	Errors in weighing or small amounts of splashed material becomes important; torque is reduced
Changes in quantity, determined by changes in coverage of the stirrer cylinder	The more fully covered the less the errors in viscosity caused when adding material	If covered too deeply, the reaction rate is greatly decreased by lack of stirring of the top layer
Changes in distance between inner and outer cylinder	A decrease in distance increases the motor response to viscosity changes; less sample needed	If distance is too low, the motor is halted by samples near the gel point
Introduction of stirring channels in the vessel wall	Improves stirring and hence reaction rate	Introduces cavitation effects which give erratic torque readings
Changes in speed of nitrogen flow	Increase speeds up reaction greatly as it aids in the removal of water	Increase causes some loss of reactants: especially volatile ones like trimethalol propane

a prepolymer/curing agent mixture for each point on the viscosity versus r curve, we have been able to start with a nongelling mixture, allow the reaction to go to completion, determine its terminal viscosity, and then add more crosslinking agent and allow the mixture to re-equilibrate to a higher viscosity. The additions are then continued until the gel point is passed. This work has indicated that it may be possible to "titrate" a prepolymer to an incipient gelation end point.

C. Binder Model Studies

Using the above techniques, a series of gelation studies were carried out with decanediol and either decanedicarboxylic acid or sebacic acid. The crosslinking agents were either 1,2,6-hexanetriol, trimethylol propane or 1,3,5-pentanetricarboxylic acid. Results obtained with the triols are not completely satisfactory: 1,2,6-hexanetriol caused the reaction mixture to darken considerably and trimethylol propane sublimed slightly out of solution. No problem was noted with the tricarboxylic acid, and the results obtained corresponded quite closely with the theoretically expected values.

Preliminary tests have also been carried out with various hydroxy- and carboxy-terminated prepolymers in an effort to determine whether the recording viscometer technique can be used to study their gelation by the esterification reaction.

Polypropylene glycol prepolymers cannot be studied, since they decompose slowly under the action of heat and p-toluenesulphonic acid catalyst. This explains the very slow rate of crosslinking observed in our previous experiments with these polymers.

Tests with a Thiokol carboxy-terminated polybutadiene prepolymer have shown that unsaturated prepolymers can be used in the gelation studies. In control runs the viscosity of samples of the prepolymer containing p-toluenesulphonic acid catalyst did not increase significantly on prolonged stirring at 135°C (under nitrogen), but when crosslinking compounds were added the viscosity increased greatly at a slightly faster rate than that of the model compounds studied previously. When sufficient

crosslinking agent was added, gelation occurred and the motor was no longer able to record viscosity. A sample of Sinclair R45, a hydroxy-terminated polybutadiene, showed anomalous behavior but the infrared spectrum indicated that it contained carboxyl groups and other impurities. Samples of Telagen S, a saturated hydroxy-terminated prepolymer from General Tire, were also tested in our apparatus with and without cross-linking triacid and was found to behave satisfactorily.

Further tests with these prepolymers have been discontinued until studies with model compounds have been completed.

IV FUTURE WORK

Experiments will be continued with a variety of model compound mixtures in an effort to fully elucidate both the theoretical and practical aspects of the recording viscometer technique for determining prepolymer functionality. Monofunctional model compounds will be included so that the results will be applicable to actual prepolymers. Detailed studies of commercially available prepolymers will be attempted only when the results with model compounds are fully understood.

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V EXPERIMENTAL

A. Procedure

For this work, a Type I system (see Appendix I) was chosen using sebacic acid, 1,10-decanediol, and 1,3,5-pentanetricarboxylic acid. The quantities of these reactants for various values of r and ρ were determined on a computer (see Appendix II), weighed on an analytical balance to within 0.1%, and placed in the reaction vessel. The mixture was melted in an oil bath and thereafter maintained at 135°C; the apparatus was then assembled and stirring was begun (see Fig. 2). A nitrogen stream was directed over the surface of the reaction to enhance water removal. After both the recorded speed and torque were constant for several minutes, p-toluenesulfonic acid catalyst was added; the speed was decreased and the torque was gradually increased. The initial stirring speed for the experiments was set at ~ 1500 RPM by adjusting the armature voltage; the initial torque was brought to zero mv on the recorder by adjusting resistor R_2 (Fig. 1).

Using this procedure, it is necessary to carry out one experiment for each desired combination of r and ρ, which is tedious and time consuming. Therefore, a technique was developed by which incremental quantities of the diol were added to the reaction mixture during the run until the mixture gelled completely. The values of r were determined by a computer from the known quantities of diol added (see Appendix III).

B. Results

The experiments produced recorder traces like that shown in Fig. 3. The speed is recorded in absolute units (RPM), but the torque is recorded in relative units (millivolts). In all cases where the mixture did not gel completely, both the speed and torque leveled off, signaling the end of the reaction.

In order to translate these data into relative viscosity, equation (6), which shows that viscosity is proportional to i/V, is used. Thus,

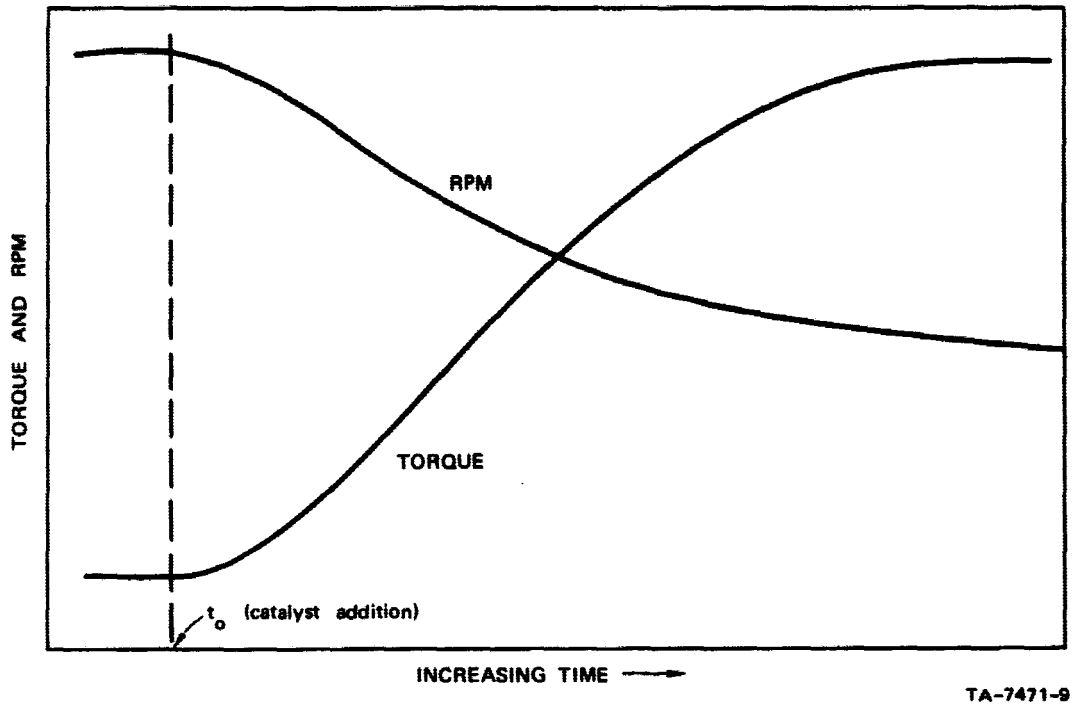


Figure 3 RECORDER TRACE

for each trace, the final torque reading is divided by the final speed in RPM/200 and a relative number is obtained for viscosity. Tables II and III show the data obtained for $\rho = 0.371$ and 0.75, respectively (in the experiments with $\rho = 0.371$, the values for r and ρ are only approximate). Figures 4 and 5 show plots of η vs r for these data; by extrapolating the straight line portion of the graphs, values of r_c (the r value at incipient gelation) are obtained.

According to Flory,[1] $\alpha = \frac{1}{2}$ is the point above which infinite chains are possible and below which they are not in a Type I gel system (see Appendix I). Thus, r_c is that value of r which, for a particular ρ, makes $\alpha = \frac{1}{2}$. Therefore, there can be no infinite chains present above r_c, and the viscosity increase in that region is due only to molecular weight increase. It is apparent that, as r approaches 1.0, the number of infinite chains present in the mixture will increase, and the viscosity will therefore increase rapidly.

Recent experiments using the sequential addition technique produced recorder traces similar to that shown in Fig. 6 ($\rho = 0.2$). The

Table II

VISCOSITY FOR $\rho = 0.371$

Experiment No.	r	Maximum Torque, mV	Final Speed, RPM/200	Viscosity (η), 200 (torque/RPM)
66	1.80	7	6.8	1.03
65	1.625	6	6.8	.88
68	1.50	12	7.2	1.67
62	1.43	16.5	7.0	2.36
67	1.39	22	6.7	3.22
64	1.35	49.5	5.7	8.68
60	1.27	103	4.6	22.5
61	1.27	107	4.8	22.3

Table III

VISCOSITY FOR $\rho = 0.75$

Experiment No.	r	Maximum Torque, mV	Final Speed, RPM/200	Viscosity (η), 200 (torque/RPM)
69	2.00	19	7.2	2.64
70	1.90	20	6.9	2.90
71	1.80	37	6.6	4.09
72	1.70	47	6.3	5.88
73	1.60	110	4.8	22.9
75	1.55	148	4.9	30.2

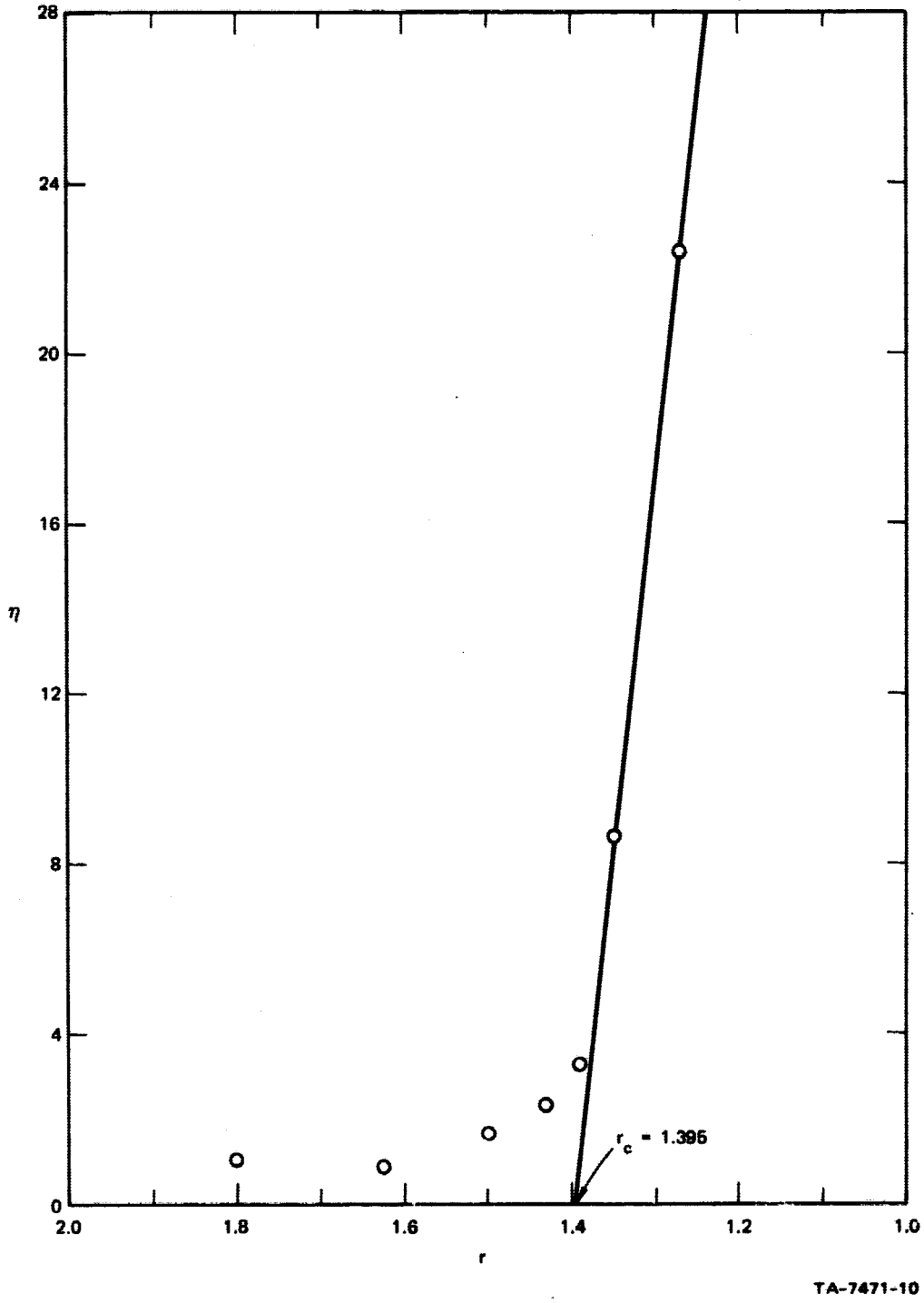


Figure 4 r VERSUS η FOR ρ = 0.371

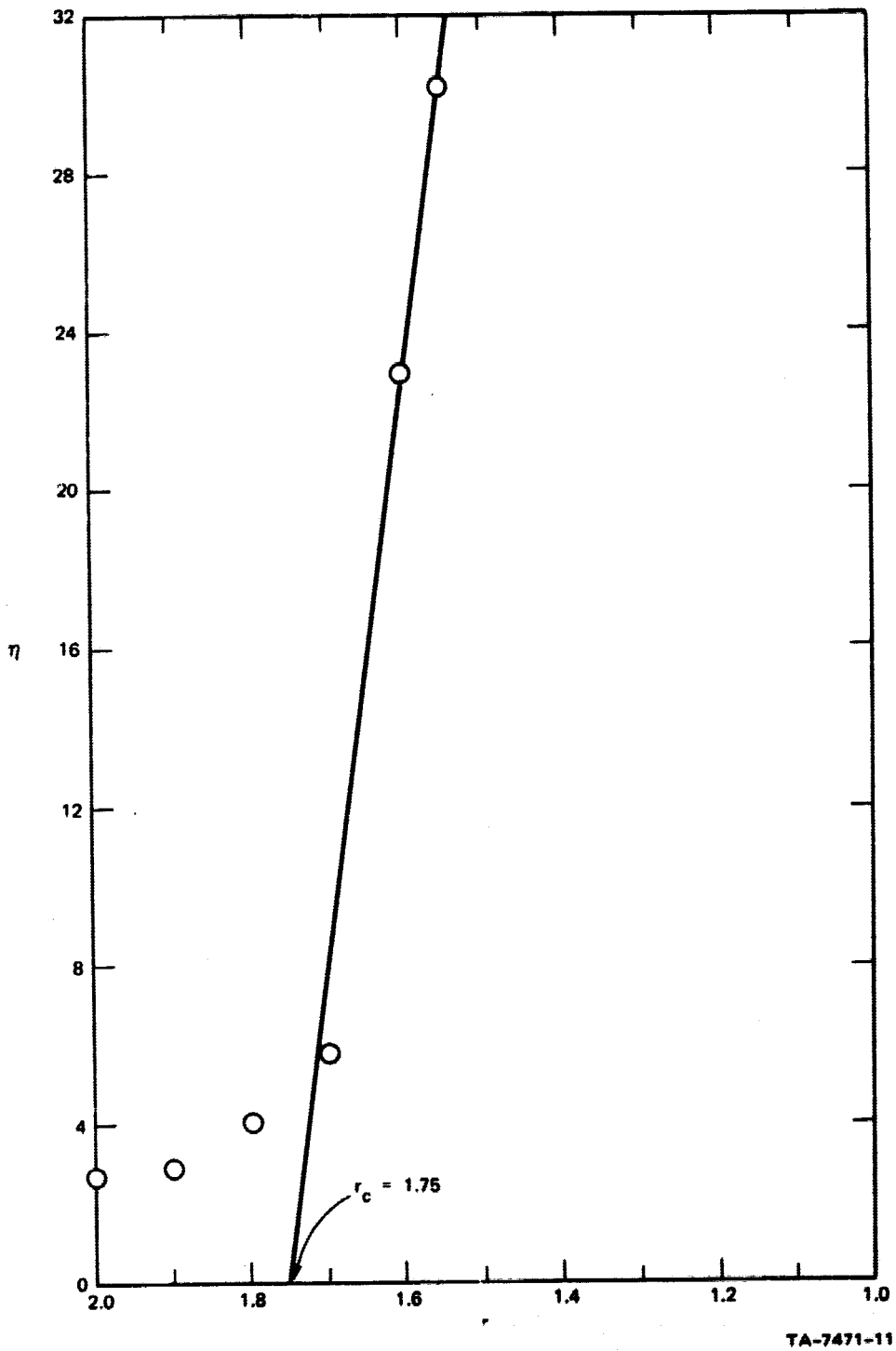


Figure 5 r VERSUS η FOR ρ = 0.75

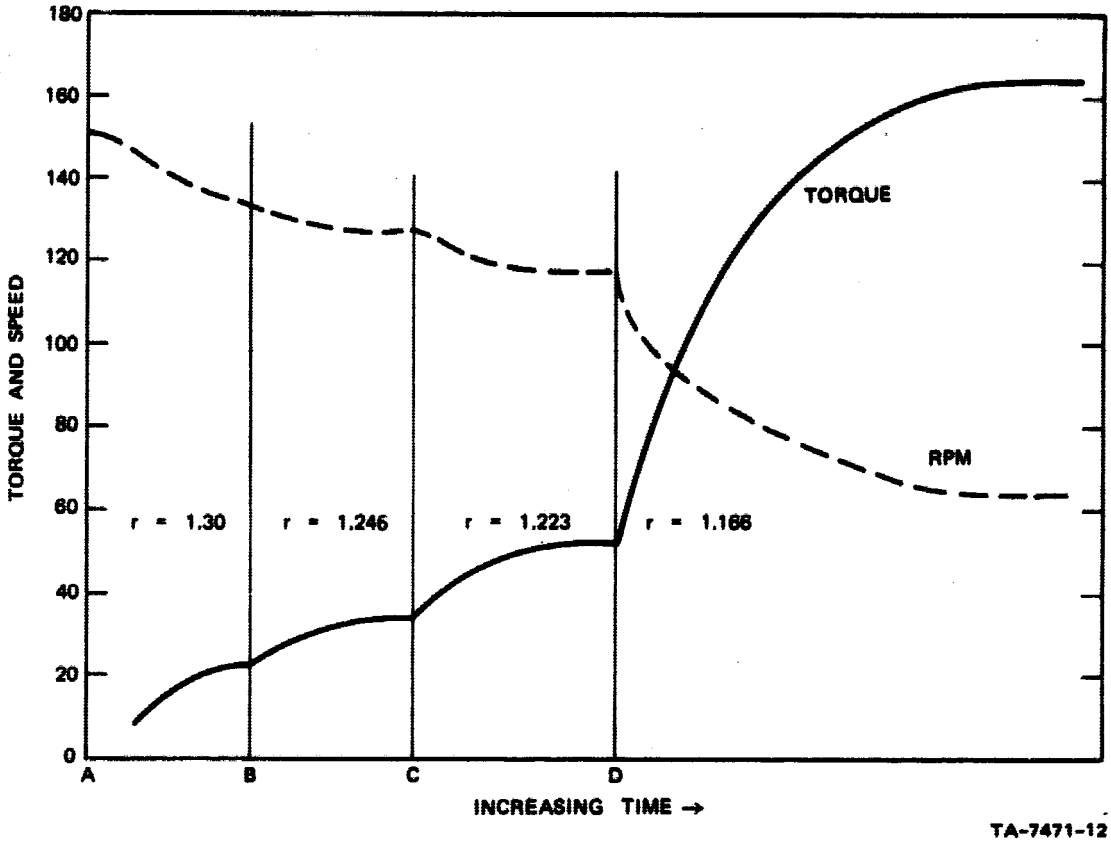


Figure 6 RECORDER TRACE

p-toluenesulfonic acid catalyst was added at point A, at which time the torque began to increase and the speed decrease; the initial value of r was 1.30. The reaction was complete at B and more diol was then added, making r = 1.246. This was repeated until, at D, r became less than r_c and a large torque increase was recorded.

Two different experiments were carried out for $\rho = 0.2$ using this technique; the results are shown in Table IV. The values of η vs r are plotted in Fig. 7. Note that the points are experimentally reproducible and yield a good r_c value.

In Fig. 8, the r_c values thus determined are plotted versus their corresponding ρ values, along with the theoretical incipient gelation line. The functionality is then calculated from these numbers using the equation

$$f = 2\left(\frac{1-\rho}{2-r_c}\right)$$

The results are shown in Table V.

Table IV

VISCOSITY FOR $\rho = 0.20$

Experiment No.	r	Maximum Torque, mV	Final Speed, RPM/200	η
77	1.40	11.5	69	1.67
77	1.348	21.9	66	3.32
77	1.306	27	65	4.15
78	1.300	22.3	67	3.33
77	1.277	32.6	63.5	5.14
78	1.264	33	64	5.16
77	1.228	53	59	8.98
78	1.223	52	59	8.81
77	1.195	96	48	20.00
78	1.166	163	32	50.9

Table V

FUNCTIONALITY AT VARIOUS ρ VALUES

ρ	r_c	f	% Error
.371	1.395	2.078	3.9
.75	1.75	2.00	0
.20	1.21	2.02	1

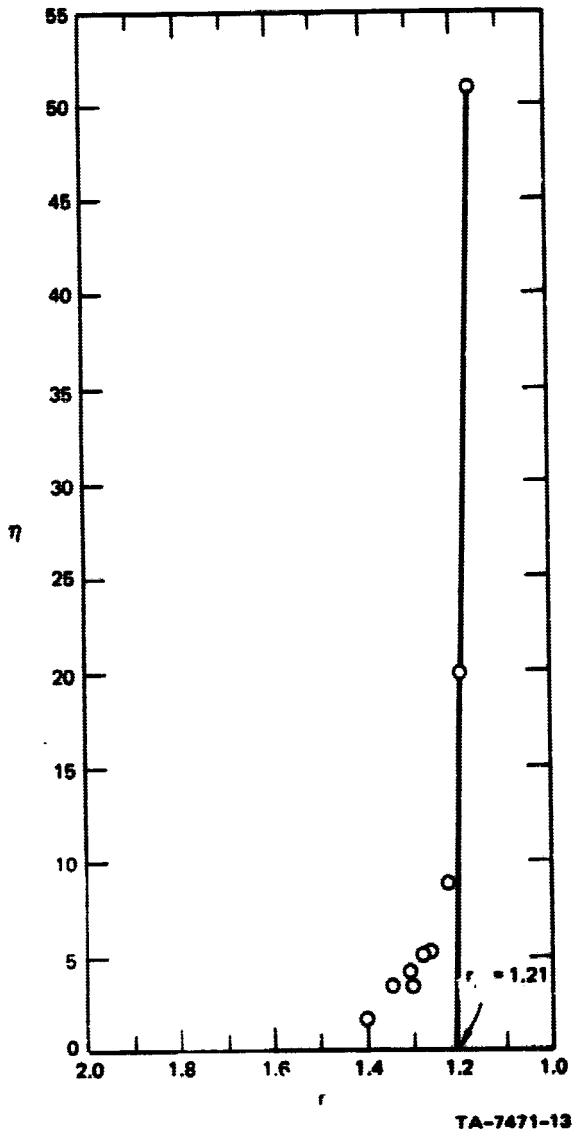


Figure 7 r VERSUS η FOR ρ = 0.20

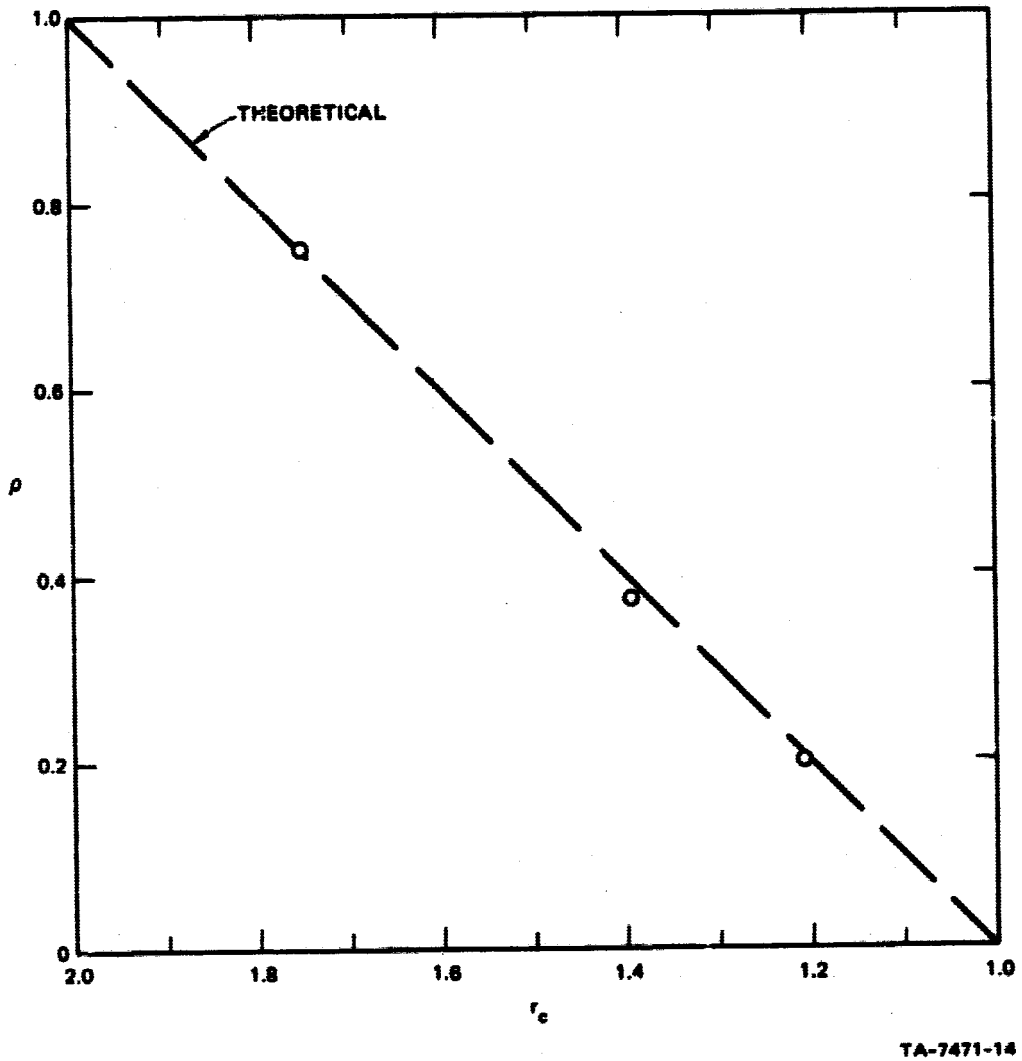


Figure 8 r_c VERSUS ρ

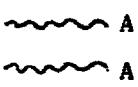
APPENDIX I

MATHEMATICAL ANALYSIS OF PREPOLYMER GELATION[1,3]

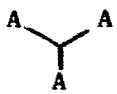
Determination of functionality is based on the calculation of the probability of an infinite network; the method of Flory[2] is used.

Consider the following prepolymer systems:

Type I



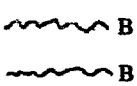
Prepolymer



B–B

Curing agents

Type II



Prepolymer

A–A

Curing agents

We make the following assumptions:

1. There are no nonfunctional species present in the prepolymer.
2. A's react only with B's and vice versa.
3. The reactivities of all A's are the same and the reactivities of all B's are the same.

We define the following for a Type I system:

P_A, P_B fraction of A's and B's, respectively, that have reacted.

ρ fraction of A's contributed by branch units to total A's.

r ratio of A's to B's.

α probability that an A from one branch unit is connected, through a polymer chain, to another branch unit.

F ratio of A's present on difunctional prepolymers to total prepolymer A's.

The probability of the formation of the chain

is given by

$$\alpha_n = P_A P_B \rho [P_A P_B (1-\rho) F]^n$$

Since we must consider all possible values of n,

$$\alpha = \sum_{n=0}^{\infty} \alpha_n = \frac{P_A P_B \rho}{1 - P_A P_B (1-\rho) F}$$

From $r = \Sigma A / \Sigma B = P_B / P_A$, we find

$$\alpha = \frac{r P_A^2 \rho}{1 - r P_A^2 F (1-\rho)} = \frac{\rho P_A^2}{R - P_A^2 F (1-\rho)}$$

where $R = 1/r$.

The corresponding expression for a Type II system is

$$\alpha = \frac{P_A^2 F \rho}{R - P_A^2 F (1-\rho)}$$

Flory has shown that, for trifunctional branch units, $\alpha > \frac{1}{2}$ is the criterion for gelation. Therefore, we take $\alpha = \frac{1}{2}$ and assume complete reaction (i.e., $P_A = 1$) to find

$$R = F + (2-F)\rho,$$

in a Type I system, and

$$R = F(\rho+1),$$

for a Type II system, at incipient gelation. From the equation

$$F = 2(1-1/f)$$

where f is prepolymer functionality, we find

$$R = 2[1 + (\rho-1)/f]$$

and

$$R = 2[(\rho+1) - (1+\rho)/f]$$

for Type I and Type II systems, respectively. These are plotted for various values of f in Figs. 9 and 10.

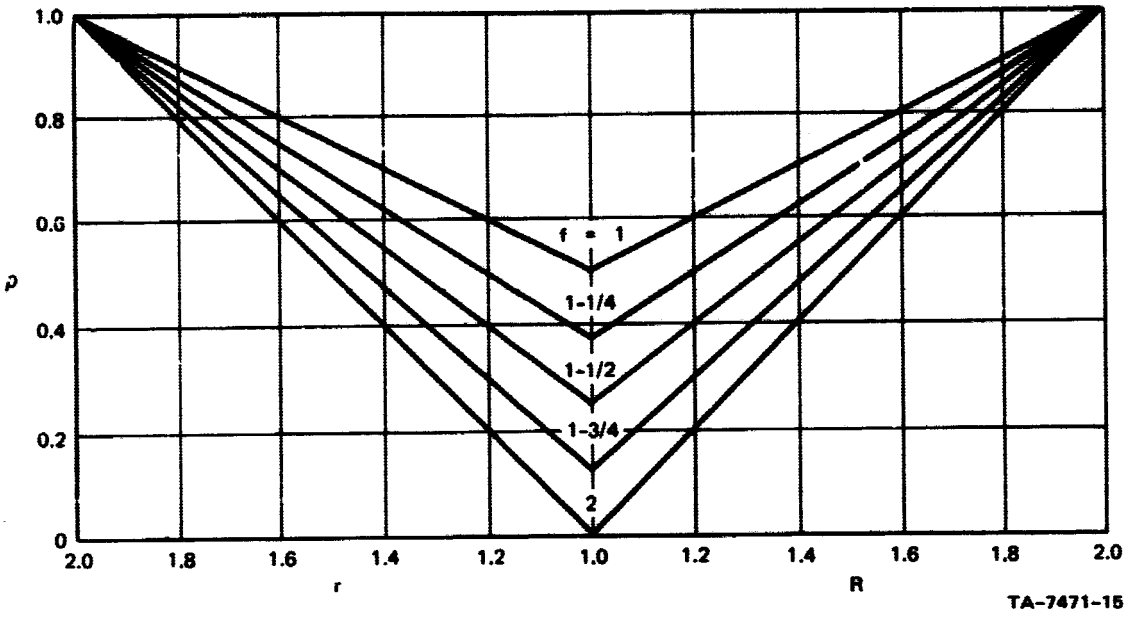


Figure 9 r VERSUS ρ FOR TYPE I SYSTEM

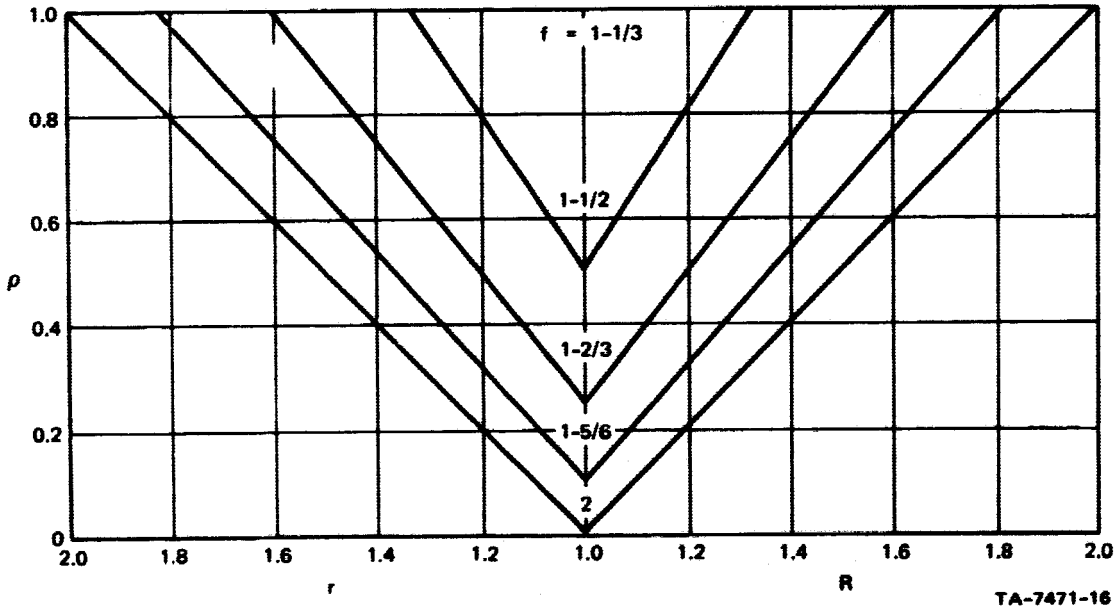


Figure 10 r VERSUS ρ FOR TYPE II SYSTEM

APPENDIX II

PROGRAMS FOR COMPUTING QUANTITIES OF MATERIALS FOR TYPE I SYSTEMS

Enter: 200 DATA A, B, C, P, W, F

where A = meq/g for triol (triacid)

B = meq/g for diol (diacid)

C = meq/g for diacid (diol)

P = ρ

W = total weight desired

F = limiting R value

```
90 REM A,B,C,P,W,F
100 PRINT "R EQUALS";R
101 PRINT
105 PRINT
110 PRINT "  R","% TRIOL","% DIOL","% DIACID"
115 PRINT
120 LET R=1
130 LET L=(A+C*R)/(A-P*P)+(P+C*R)/(P*P)
140 LET A= (C*R*W)/(P-P*P)/L
150 LET I=(C*R*W)/(P+L)/P
160 LET Z=W-A-I
170 PRINT R,A,I,Z
180 LET R=R+.05
190 IF R>F THEN 999
195 GOTO 130
200 DATA 14.7,9.9,11.5,.95,25,2.5
999 END
```

APPENDIX III

PROGRAM FOR COMPUTING r FROM THE ADDITION OF DIOL TO TO A DI-TRI ACID MIXTURE

Enter: 100 DATA A, C, X, P

where A = meq/g triacid

C = meq/g diol

X = g triacid

P = ρ

200-300 DATA Z

where Z = grams of diol added

```
90 READ A,C,X,P
100 DATA 14.7,11.5,7.33097,.6
105 PRINT "G DIOL","  R"
106 PRINT
110 LET D=A*X/P
120 READ Z
130 LET R=D/(C*Z)
140 PRINT Z,R
150 GO TO 120
200 DATA 10.41,10.5,11.0,11.5,12.0,12.5
999 END
```

REFERENCES

1. Flory, P. J., J. Am. Chem. Soc., 63, 3083 (1941).

2. Flory, P. J., J. Am. Chem. Soc., 62, 1057 (1940).

3. Marsh, H. E., private communication.

4. Mysels, K. J., "Introduction to Colloid Chemistry," Interscience, 1965, p. 256.

LABOR AND FINANCIAL STATUS REPORT

The labor and financial status of the project as of 22 February 1969 was as follows: 8.7 man-months of effort and a total of $23,061 have been spent since the commencement of the program. Funds committed but not spent amount to $80.00. Funds remaining amount to $21,692.